

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(57) Abstract: The invention relates to a method of preventing hydrate formation by reinjecting hydrocarbon gas from an oil production in a production well. Part of the hydrocarbon gas stream from the oil production is reacted to produce raw methanol. This is subsequently added to the remaining hydrocarbon gas which is reinjected in the same production well or injected in another production well. The invention also relates to the use of a slip stream from a hydrocarbon gas stream separated from oil in the production of oil in a production well for the synthesis of methanol to be added to the remaining hydrocarbon gas stream to prevent the formation of hydrocarbon gas hydrates when said hydrocarbon gas stream is reinjected in oil production wells.

Method and system for preventing hydrate formation by reinjecting hydrocarbon gas including methanol

Background of the invention

5 The present invention relates to a method of preventing hydrate formation when transporting untreated hydrocarbon gas. The invention relates to the use of a slip stream from a hydrocarbon gas stream separated from oil in the production of oil in a production well for the synthesis of methanol to be added to the remaining hydrocarbon gas stream to prevent the formation of hydrocarbon gas hydrates when said hydrocarbon gas stream is to be further
10 transported.

When hydrocarbon gas is subjected to high pressures and low temperatures in the presence of water in liquid or gaseous form hydrocarbon hydrates in the form of solid products can be formed. If such hydrates are formed in sufficient high amounts they can clog pipelines in which the gas is flowing and thereby prevent the intended gas flow.

15 In the production of crude oil most reservoir fluids also produce associated gas. In order to meet the crude oil specification with respect to flash point, the gas must be flashed off from the crude oil through a sequence of separation steps.

It is possible to utilize the gas from these separation steps as a fuel gas. However, in most cases a surplus of gas compared to the required fuel gas is produced thereby.

20 For new field development in remote areas gas pipeline infrastructure is normally not present close to the production area to which the gas could be exported. Neither would the field economy allow for installing a new pipeline of any length. Consequently, the gas must be flared or reinjected into the reservoir at an injection pressure ranging normally from 250-350 bar to enhance the production of further oil. In most developed country areas flaring of
25 larger amount of gas would not be permitted due to resource and environmental considerations.

Prior to the injection of such gas the gas has to be compressed. The water dew point is controlled by the use of glycol dehydration towers. The dehydration is performed to remove free water to eliminate the possibility of hydrate formation when the gas is cooled.

30 The dehydration systems comprise at least one stripper column wherein the gas is countercurrently contacted with the glycol stripping the water from the gas into the glycol phase. The water rich on glycol is then transferred to a glycol reboiler in which the water is stripped off and the glycol stripped of water is recycled to the above mentioned at least one

stripping column. The system for processing the glycol comprises several heat exchanges, degassing vessels, pumps etc..

Thus, the glycol system must be considered as a heavy system contributing severely to the costs of gas treatment and compression.

5 Thus, based on a flow of four MMSCMD of gas, the gas treatment (dehydration) cost is estimated to:

80-90 MNOK

85-90 tonnes.

The dehydration plant also has a high OPEX cost due to its complexity and continuous
10 need for make-up glycols.

An alternative to the dehydration of gas to prevent hydrate formation is the use of chemicals.

The conventional chemicals used for this purpose are methanol, monoethylene glycol, diethylene glycol and three ethylene glycol. The addition of chemicals, specifically methanol
15 and ethylene glycol, is disclosed in E.D. Sloan Jr., Clathrate Hydrates of Natural Gases, Marcel Dekker, Inc., New York, 1998, pp 164-170. These antifreezes expand the pressure-temperature-area of the safe operation. However, large quantities thereof are required, and 50% of such additives in the water liquid fraction is not unusual in productions rich on water. The use of methanol in the North Sea may thus approach 3 kg per 1000 Sm³ of gas extracted.
20 This implies severe demands on the logistics of the transport and storage.

There is thus a strong need of providing a more economic way of preventing the formation of gas hydrates when the gas from oil production is reinjected in oil formations.

25 **Summary of the invention**

The object of the present invention is thus to provide a more economic and efficient way of preventing the formation of gas hydrates during transport of gas and/or reinjection of gas.

The problem is solved by using part of the gas separated from the oil produced in an
30 oil production well for the production of a dirty (impure) methanol which is combined with the rest of the gas stream, which combined stream is subjected to gas compression and exported or reinjected into a suitable reservoir.

Thus, the present invention provides a method of preventing hydrate formation by reinjecting hydrocarbon gas from an oil production in a production well, wherein part of the

hydrocarbon gas stream from the oil production is reacted to produce raw methanol, which is subsequently added to the remaining hydrocarbon gas which is reinjected in the same production well or injected in other production wells.

According to one embodiment of the invention said part of the hydrocarbon gas stream
5 from the oil production is split off from the main stream of the hydrocarbon gas and fed to a methanol synthesis plant separate from the main stream, to which steam and the energy required is supplied, said plant having a downstream connection back to the main stream.

According to another embodiment of the invention said part of the hydrocarbon gas stream is fed to a methanol synthesis plant situated integrated in the main hydrocarbon stream,
10 to which steam and the energy required is supplied, the product of which synthesis being discharged in the main stream flowing by.

One option of this embodiment involves that the methanol synthesis plant is located subsea.

Another option thereof involves that the methanol synthesis plant is located onboard a
15 production platform or on board a vessel.

A further aspect of the instant invention relates to a method of preventing hydrate formation by reinjecting hydrocarbon gas from an oil production in a production well, wherein oil and hydrocarbon gas from an oil production is reacted in a subsea methanol synthesis plant to produce raw methanol, which is subsequently added to hydrocarbon gas
20 which is reinjected in the same production well or injected in another production well. MeOH will be hydrofile and hence suitably be dissolved in water.

In the above mentioned methods said part of the hydrocarbon gas stream is preferably converted to methanol by a sequence of a reformation reaction and a Fischer Tropsch
25 reaction.

Particularly the reformation reaction is performed in the presence of a reformation catalyst, at a low pressure of about 5 to 50 bar, and an outlet temperature of about 400 to 650 °C in the absence of O₂.

A commercially available reforming catalyst may be used.

30 The methanol synthesis may be effected by feeding a synthesis gas comprising mainly hydrogen and carbon monoxide to a methanol synthesis reactor run e.g. at a temperature of between 170 °C and 240 °C and at a pressure of between 5 and 20 MPa in the presence of a catalyst based on Zn and Cu oxides, such as the catalyst sold by Haldor Topsøe A/S, Denmark, under the trade-name "MK-101". Such a synthesis is disclosed in US Patent No.

5,262,443 to Haldor Topsøe A/S, which is incorporated herein by reference. However also any other commercial methanol synthesis may be used.

Further the present invention relates to the use of a slip stream from a hydrocarbon gas stream, separated from an oil in the production of oil in a production well, for the synthesis of
5 methanol to be added to the remaining hydrocarbon gas stream to prevent the formation of hydrocarbon gas hydrates when said hydrocarbon gas stream is reinjected in oil production wells.

According to one option thereof said part of the hydrocarbon gas stream from the oil production is split off from the main stream of the hydrocarbon gas and fed to a methanol
10 synthesis plant separate from the main stream, to which steam and the energy required is supplied, said plant having a downstream connection back to the main stream.

According to another option thereof said part of the hydrocarbon gas stream is fed to a methanol synthesis plant situated integrated in the main hydrocarbon stream, to which steam and the energy required is supplied, the product of which synthesis being discharged in the
15 main stream flowing by.

The last option involves that the methanol synthesis plant may be located subsea.

Further the methanol synthesis plant may be located onboard a production platform or onboard a vessel.

The present invention also relates to the use of the lower molecular hydrocarbon part
20 of an oil and hydrocarbon gas mixture for the production of methanol to be used for preventing hydrate formation when reinjecting hydrocarbon gas from an oil production in a production well, wherein oil and hydrocarbon gas from an oil production is reacted in a subsea methanol synthesis plant to produce raw methanol, which is thereby dissolved in the produced water, which is subsequently added to hydrocarbon gas which is reinjected in the
25 same production well or injected in another production well.

Preferably said part of the hydrocarbon gas stream is converted to methanol by a sequence of a reformation reaction and a Fischer Tropsch reaction.

Particularly the reformation reaction is performed in the presence of a reformation catalyst, at a low pressure of about 5 to 50 bar, and an outlet temperature of about 400 to 650
30 °C in the absence of O₂.

Most preferably the pressure is kept at about 20 bar and the temperature is kept at about 650 °C.

A commercially available reformation catalyst can be used for this purpose.

Detailed description of the invention.

Any well know feasible synthesis of methanol can be used in this connection. Suitably processes will be used which are easily to adapt to the environment of a production platform, and the plant for carrying out such a production is easy to build on a production platform.

Preferably said part of the hydrocarbon gas stream is converted to methanol by a so called "black box" comprising a sequence of reformation reaction and Fischer Tropsch reaction.

Preferably the reformation reaction is performed at a low pressure of about 20 bar and an outlet temperature of about 650°C in the absence of O₂.

Such a plant which is required for effecting said processes would be situated on a production platform. Thus, no transport or storage logistic requirements will be involved.

Usually sufficient high pressure hydrocarbon gas and some fresh water would be available for effecting the reformation reaction. The reaction is normally performed in the presence of a reformation catalyst.

The subsequent Fisher Tropsch reaction can be effected under the usual Fischer Tropsch reaction conditions (useful temperature intervals and pressure intervals should be defined) and catalysts (some examples should be mentioned).

In this process the quality and degree of the methanol conversion has an limited impact on the overall process. The formation of possible side products is not critical, as such products will be injected into the reservoir. The absence of purification requirement in connection with this method of preventing hydrate formation is a significant contribution to the economics of the total process.

A further advantage of the method of the present invention is the elimination or at least reduction of omission of glycol, volatile organic compounds and ETEx from a glycol reboiler. On conventional offshore plants one of the greatest contributions to hydrocarbon emission outside the power generation is normally the glycol reboiler system. The instant method of the invention thus provides a significant contribution to the reduction of pollution of the environment.

Brief Explanation of the Figures

The enclosed figures shows the plants used for performing the method of the invention integrated in an oil production and gas injection stream.

Figure 1 shows the conversion of a slip gas stream from a hydrocarbon main stream being converted to methanol in an isolated "black box", the dirty methanol obtained

subsequently being reintroduced in the hydrocarbon main stream downstream, whereupon said methanol containing hydrocarbon main stream is injected in an oil reservoir.

Figure 2 shows the conversion of part of a hydrocarbon main gas stream being converted to methanol in an isolated "black box" within a hydrocarbon main stream pipeline
5 topside the sea surface, the dirty methanol obtained subsequently being reintroduced in the hydrocarbon main stream downstream, whereupon said methanol containing hydrocarbon main stream is injected in an oil reservoir.

Figure 3 shows the conversion of part of a hydrocarbon main stream comprising oil and gas being converted to methanol in an isolated "black box" within a hydrocarbon main
10 stream pipeline subsea, the dirty methanol obtained subsequently being reintroduced in the hydrocarbon main stream downstream, whereupon said methanol containing hydrocarbon main stream is injected in an oil reservoir (not shown on this figure).

Figure 4 shows the conversion of part of a hydrocarbon main gas stream being converted to methanol in an isolated "black box" within a hydrocarbon main stream pipeline
15 subsea, the dirty methanol obtained subsequently being reintroduced in the hydrocarbon main stream downstream, whereupon said methanol containing hydrocarbon main stream is injected in an oil reservoir (not shown on this figure).

Detailed Description of the Invention

The object of the present invention is to provide a more economic and efficient way of
20 preventing the formation of gas hydrates for evacuation/transport of hydrocarbon gas.

The problem is solved by using part of a flowing hydrocarbon (HC) gas for the production of a dirty (impure) methanol, which is combined with the rest of the gas stream thus preventing hydrates to form.

Thus, the present invention provides a method of preventing hydrate formation
25 wherein part of the hydrocarbon gas stream from the oil production is reacted to produce raw methanol. The methanol is subsequently added to the remaining hydrocarbon gas stream which will be transported or injected into one or more suitable reservoirs.

Any well known feasible synthesis of methanol can be used in this connection. Suitably processes will be used which are easily to adapt to the environment of a hydrocarbon
30 treatment centre, and the plant for carrying out such a production is based on proven technology.

Preferably said part of the hydrocarbon gas stream is converted to methanol by a MeOH converter, comprising a sequence of reformation reaction and Fischer Tropsch reaction.

Depending on size and complexity, the location of the MeOH converter could be:

- On its own with the required interfaced for feedstreams and MeOH injection Ref. fig. 1
- 5 - inline piping on top side – Ref. fig. 2.

Depending on the requirement for single gas phase operation, subsea installation of a MeOH converter to ensure flow assurance might be possible. If single gas phase operation will be required for the MeOH converter operation, a combination of subsea separation and
10 MeOH conversion is possible.

- Installed inline in the pipeline or the flowline – Ref. fig. 3.
- Installed in sequence with subsea separation – Ref. fig. 4.

15 Any well known reformation reaction conditions may be used. Preferred reaction conditions are, however, the SOLCO TEPS conversion of nature gas to methanol system. This involves a low pressure system of about 20 bar, a low outlet temperature of about 650°C, whereas other reformers/reactors typically utilise temperatures of 1000-1200°C. Further, only limited amount of steam input is required in addition to the hydrocarbon gas fed to the
20 process. No oxygen gas or carbon-dioxide is required. In fact, this SOLCO process yields a quality which is superior to what the dirty methanol operation requires.

Thus, no transport or storage logistic requirements will be involved.

Since the quality and degree of the methanol conversion in this proposal has a limited impact on the overall process, the final pressure and temperature might be altered to fit the
25 given condition present. The formation of possible side products is not critical, as such products will be exported or injected into a reservoir. The absence of purification requirement in connection with this method of preventing hydrate formation is a significant contribution to the economics of the total process. The SOLCO TEPS methanolisation process could also be optimized by selecting a higher pressure on the feed gas.

30 The optimal solution is the conversion of the free water in the gas, thus providing for a self-inhibition by the methanol generation thereby only requiring the reactors, catalysts and pressure.

A further advantage of the method of the present invention is the elimination of emission of glycol, volatile organic compounds and BTEX from a glycol reboiler. On

conventional offshore plants one of the greatest contributions to hydrocarbon emission outside the power generation is normally the glycol reboiler system. The instant method of the invention thus provides a significant contribution to the reduction of pollution of the environment.

5 The enclosed figure 1 shows a typical plant used for performing the method of the invention integrated in an oil and gas production with a gas injection stream.

Thus, a mixture of oil and gas is produced from an oil reservoir. This is subjected to an oil and gas separation in a plant as indicated in the figure. The gas fraction separated is transferred to a gas compression train. The outlet gas stream 1 from the compressor train is
10 split into two streams of which a slip stream 2 is fed to a MeOH converter, comprising one or more reformation reactors and one or more Fischer Tropsch reactors. The slip stream hydrocarbon gas is together with steam fed to the reformation reactors. The required energy is also fed to the system.

The product stream 4 is combined with the remaining hydrocarbon gas stream 1 and
15 fed to a gas compressor. The pressurised composition comprising the dirty methanol is then injected in an export solution preventing formation of hydrocarbon hydrates prone to plugging the injection gas pipelines.

Based on a flow rate of 4 MMSCMD and an efficiency of 50% conversion in the reactor, a slip stream 2 of 3500 SM³ gas is required on a daily basis for the required methanol
20 conversion to prevent hydrocarbon hydrate formation. Additionally, 2 tonnes of steam is required. The energy supply 5 will be required only in sufficient amounts to achieve the sufficient reaction temperature.

The concept of the invention is defined in the appending claims.

We claim:

1. A method of preventing hydrate formation by reinjecting hydrocarbon gas from an oil production in a production well, which hydrocarbon gas being fed methanol, wherein part
5 of the hydrocarbon gas stream from the oil production is reacted to produce raw methanol, which is subsequently added to the remaining hydrocarbon gas, which hydrocarbon gas including methanol is reinjected in the same production well or injected in another production well.
- 10 2. The method of claim 1, wherein said part of the hydrocarbon gas stream from the oil production is split off from the main stream of the hydrocarbon gas and fed to a methanol synthesis plant separate from the main stream, to which steam and the energy required is supplied, said plant having a downstream connection back to the main stream.
- 15 3. The method of claim 1, wherein said part of the hydrocarbon gas stream is fed to a methanol synthesis plant situated integrated in the main hydrocarbon stream, to which steam and the energy required is supplied, the product of the synthesis being discharged in the main stream flowing by.
- 20 4. The method of claim 3, wherein the methanol synthesis plant is located subsea.
5. The method of claim 3, wherein the methanol synthesis plant is located on a production platform or on a vessel.
- 25 6. A method of preventing hydrate formation by reinjecting hydrocarbon gas from an oil production in a production well, which hydrocarbon gas being fed methanol, wherein oil and hydrocarbon gas from an oil production is reacted in a subsea methanol synthesis plant to produce raw methanol, which is subsequently added to hydrocarbon gas, which hydrocarbon gas including methanol is reinjected in the same production well or injected
30 in another production well.
7. The method of the claims 1-6, wherein said part of the hydrocarbon gas stream is converted to methanol by a sequence of a reformation reaction and a Fischer Tropsch reaction.

8. The method of claim 7, wherein the reformation reaction is performed in the presence of a reformation catalyst, at a low pressure of about 5 to 50 bar, and an outlet temperature of about 400 to 650 °C in the absence of O₂.
- 5 9. The method of claim 8, wherein the pressure is kept at about 20 bar and the temperature is kept at about 650 °C.
- 10 10. A system for the production of oil and gas from a production subsea well and combined with the reintroduction of at least part of the gas into an oil production well without plugging of the pipelines by the formation of gas hydrates, comprising production lines (1), a "black box" comprising one or more reformation reactors having a steam or water supply (3) and an energy supply (5), and one or more methanol production reactors,
- 15 optionally a pipeline (4) therefrom back to the pipeline (1) downstream, further downstream gas compression means and pipelines for reinjection of the gas into production wells.
11. The system of claim 10, which further includes oil and gas separation means between the
- 20 production well and the "black box".
12. The system of claim 10, wherein the "black box" is located outside the production pipeline (1) having a hydrocarbon gas slip stream supply (2).
- 25 13. The system of claims 10 and 11, wherein the "black box" is located inside the production pipeline 1.

Figure 1

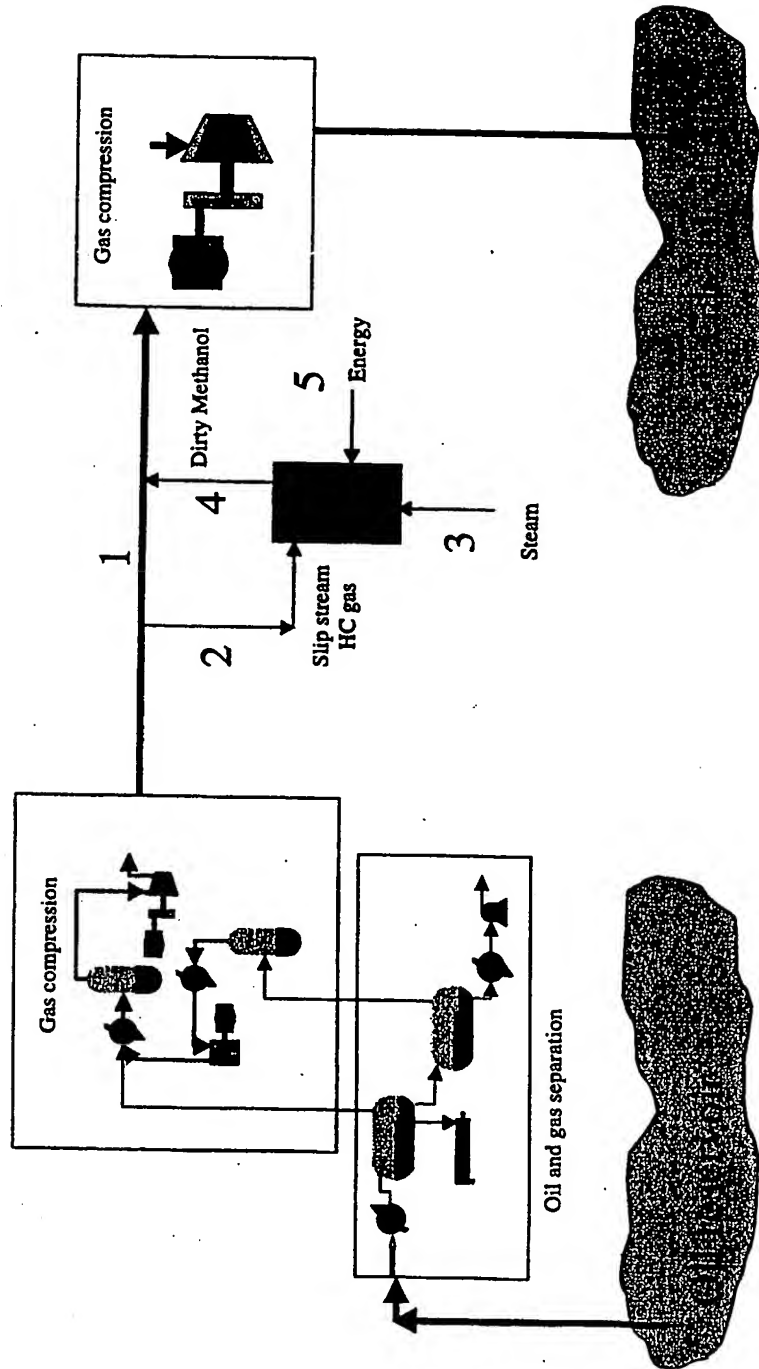
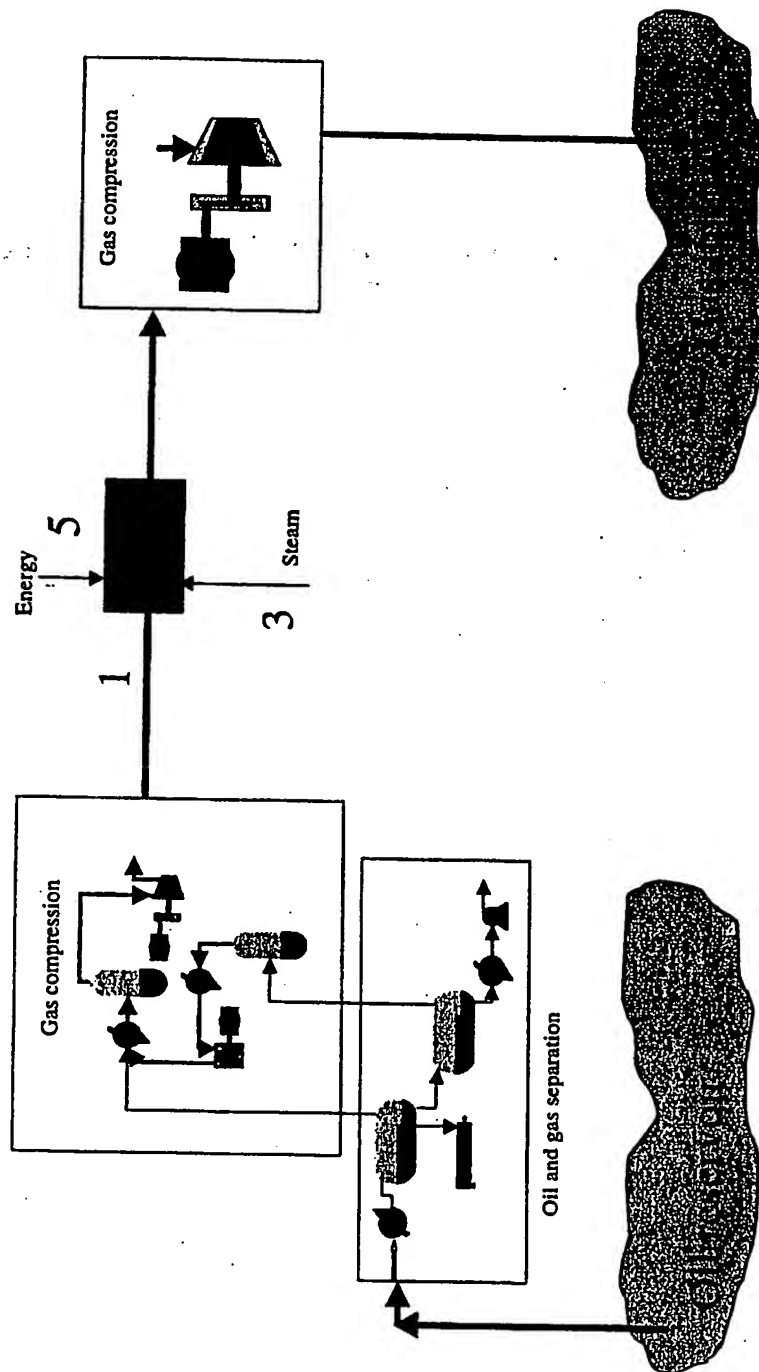
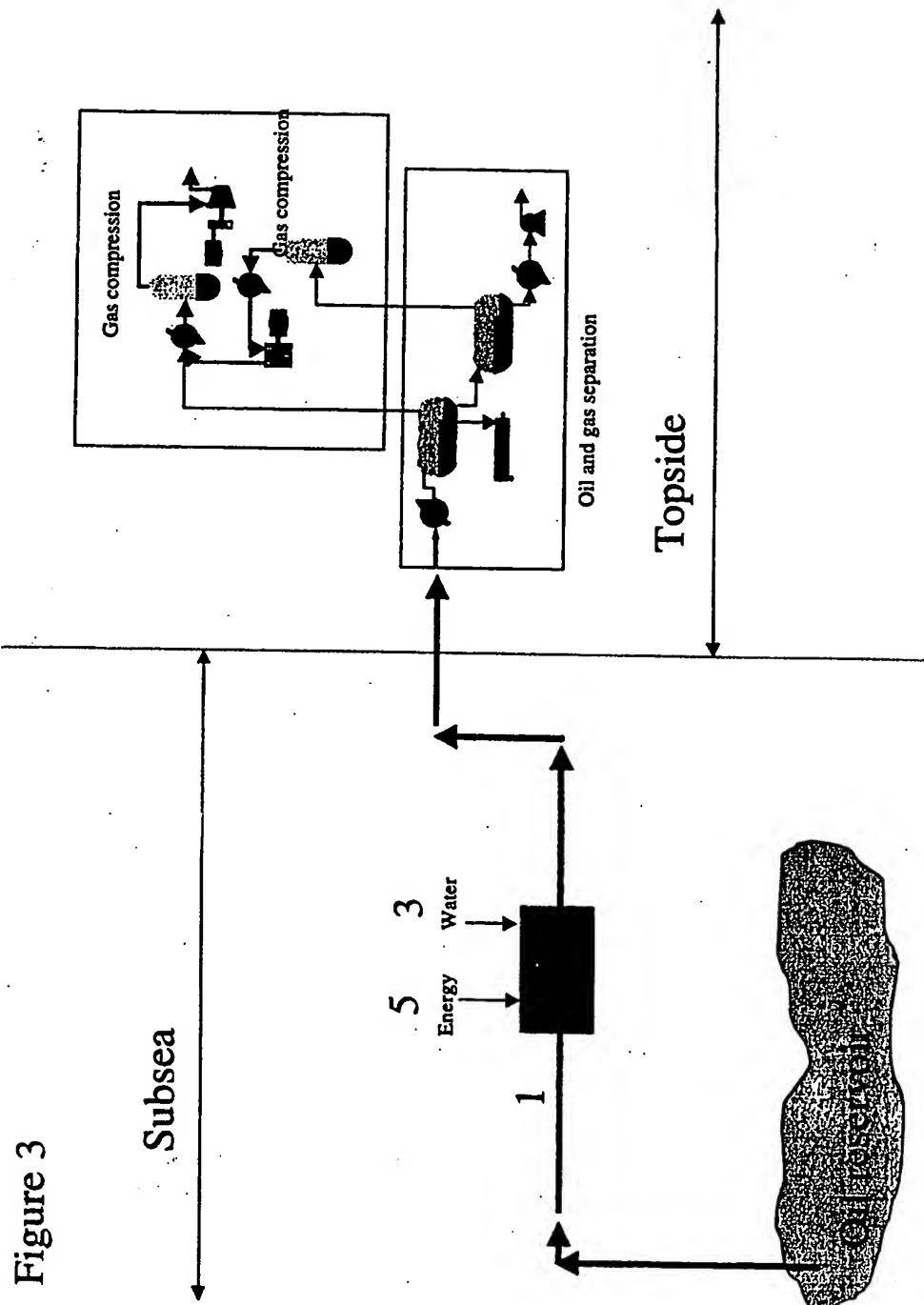
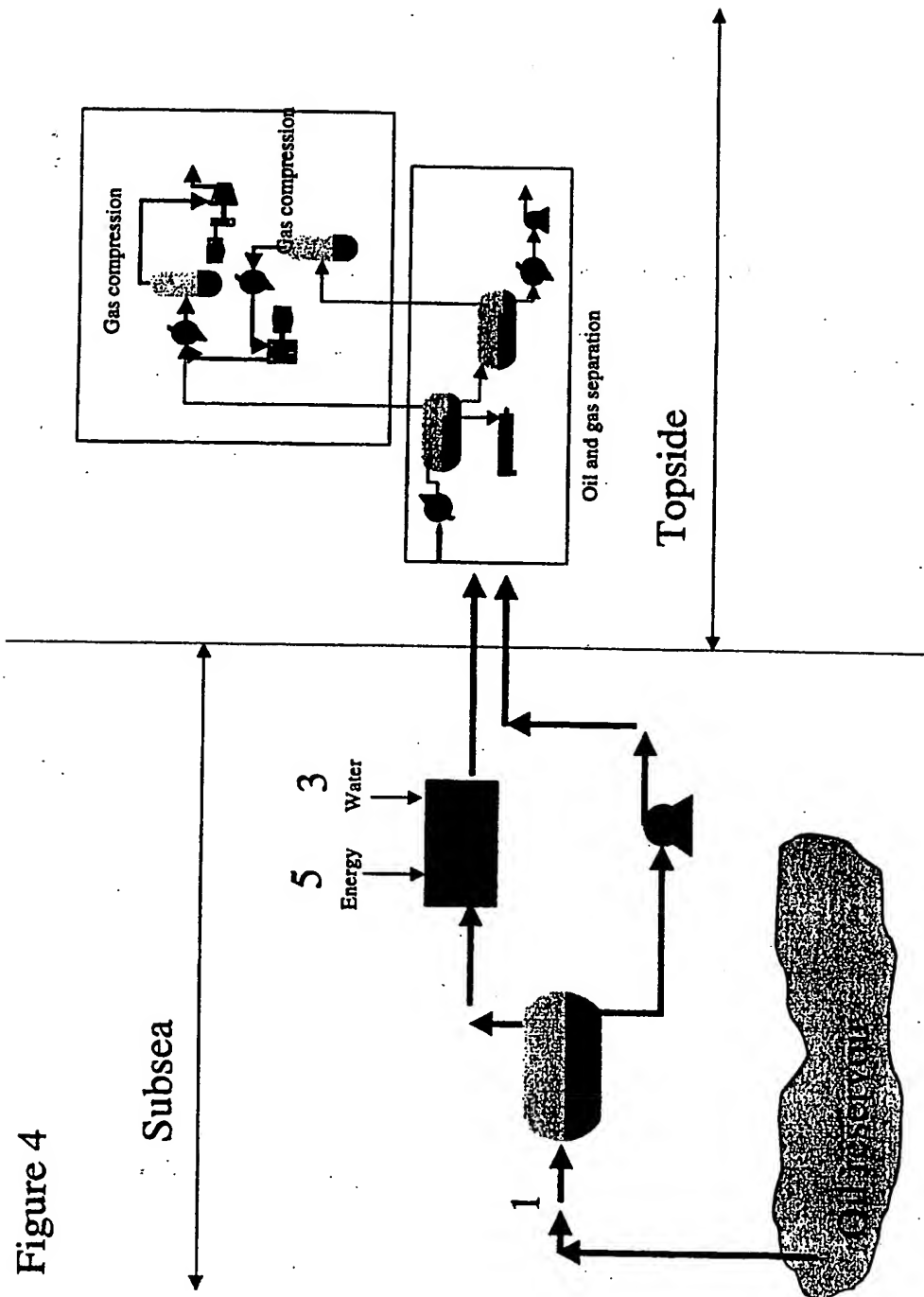


Figure 2







INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 00/00395

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: E21B 37/06, E21B 43/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO 0040835 A1 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.), 13 July 2000 (13.07.00)	1-13
	--	
A	US 4036247 A (B.F. BAUGH), 19 July 1977 (19.07.77)	1-13
	--	
A	US 3348614 A (J.A. SINLAIR ET AL), 24 October 1967 (24.10.67)	1-13
	--	
A	GB 2255102 A (KVAERNER SUBSEA CONTRACTING A/S), 28 October 1992 (28.10.92)	1-13
	--	

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

28 March 2001

30-03-2001

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Christer Bäcknert / MRo
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 00/00395

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5262443 A (H.F.A. TOPSOE ET AL), 16 November 1993 (16.11.93) -- -----	1-13

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/NO 00/00395

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
WO	0040835	A1	13/07/00	AU	2104500 A	24/07/00
				AU	2434700 A	24/07/00
				WO	0040338 A	13/07/00
				AU	3044600 A	24/07/00
				WO	0040834 A	13/07/00

US	4036247	A	19/07/77	NONE		

US	3348614	A	24/10/67	NONE		

GB	2255102	A	28/10/92	GB	9108543 D	00/00/00
				NO	900500 A	05/08/91

US	5262443	A	16/11/93	AT	139222 T	15/06/96
				AU	632406 B	24/12/92
				AU	7351391 A	19/09/91
				CA	2038530 A	20/09/91
				CN	1028096 B	05/04/95
				CN	1055730 A	30/10/91
				CS	9100722 A	15/10/91
				CZ	280489 B	17/01/96
				DE	69120118 D,T	24/10/96
				DK	71090 A	20/09/91
				DK	163578 B,C	16/03/92
				EP	0448019 A,B	25/09/91
				SE	0448019 T3	
				ES	2090159 T	16/10/96
				JP	2030834 C	19/03/96
				JP	4217635 A	07/08/92
				JP	7029960 B	05/04/95
				PL	289475 A	24/02/92
				SU	1838289 A	30/08/93
				ZA	9102025 A	24/12/91
